

Claims

We claim:

1. A method for extracting manganese from an aqueous solution containing iron, comprising the steps of:

extracting the manganese and iron by contacting the aqueous solution with a QL reagent, wherein said QL reagent comprises a quaternary ammonium compound, a hydrogen ion exchange reagent and an organic solvent, such that an organic phase containing the manganese and iron and an aqueous phase are formed;

stripping the manganese and iron from the organic phase by contacting the organic phase with acid, such that the manganese and iron shift from the organic phase to the aqueous phase;

removing the iron from the aqueous phase by oxidizing the iron, such that the iron precipitates leaving a supernatant containing the manganese; and

electrowinning the supernatant, such that electrolytic manganese dioxide deposits on the anode.

2. The method of claim 1, wherein in step (a) the pH of the solution remains constant.

3. The method of claim 2, wherein the pH of the solution is at least 1.5.

4. The method of claim 1, wherein calcium is extracted from the aqueous solution of step (a) in an intermediate step, comprising the steps of introducing manganese-rich strip solution to the organic phase of step (a); displacing calcium from the organic phase; and scrubbing the displaced calcium from the solution.

5. The method of claim 4, wherein the manganese-rich strip solution comprises a side-stream of recycled electrolyte.

6. The method of claim 4, wherein the manganese-rich strip solution contains an organic phase/aqueous phase (O/A) ratio between 5-20.

7. The method of claim 6, wherein the O/A ratio is 10.

8. The method of claim 1, wherein the aqueous solution is geothermal brine.

9. The method of claim 8, wherein the geothermal brine contains zinc which is removed from the aqueous solution, during step (a), through a step comprising,

contacting the aqueous solution with a QL reagent to create a mixture, wherein said QL reagent comprises a quaternary ammonium compound and a hydrogen ion exchange reagent; and

contacting the mixture with pure H₂O.

10. The method of claim 1, wherein during the stripping step the organic phase is neutralized and washed to reform the components of the QL reagent, comprising

contacting the organic phase with a solution comprised of sodium hydroxide;

allowing the aqueous phase and organic phase to separate, then discarding the aqueous phase; and

adding di-butyl butyl phosphonate (DBBP) to the organic.

11. The method of claim 10, wherein the organic phase and sodium hydroxide solution are contacted in an O/A ratio of 1.

12. The method of claim 10, wherein the organic phase is contacted with a sodium chloride solution or Na₂SO₄ solution.

13. The method of claim 1, wherein a phase modifier is added to step (a).

14. The method of claim 13, wherein the phase modifier is DBBP.
15. The method of claim 1, wherein the supernatant in step (d) is comprised of manganese chloride.
16. The method of claim 1, wherein step (a) is performed in at least one column comprising a closed and pressurized vesicle with fillers contained therein.
17. The method of claim 16, wherein multiple columns are connected in a series such that the product of one column may be transferred to the next for further extraction.
18. The method of claim 16, wherein the column is maintained at a positive air pressure with nitrogen, another inert gas or steam.
19. The method of claim 1, wherein all components of the extraction step are performed under anoxic conditions.
20. The method of claim 1, wherein the organic solvent is selected from the group comprising an aliphatic or aromatic hydrocarbon.
21. The method of claim 20, wherein the organic solvent is a chlorinated hydrocarbon.
22. The method of claim 20, wherein the organic solvent is heptane.
23. The method of claim 1, wherein the quaternary ammonium compound is tricapryl methylammonium chloride.
24. The method of claim 1, wherein the hydrogen exchange reagent is diethylhexylphosphate.

25. The method of claim 1, wherein the acid in step (b) is a non-oxidizing acid.
26. The method of claim 25, wherein the non-oxidizing acid is hydrochloric acid or sulfuric acid.
27. The method of claim 1, wherein in step (c) the pH of the aqueous phase is between 2-5.
28. The method of claim 1, wherein calcium is further extracted during the stripping step.
29. The method of claim 1, wherein the iron is oxidized with an oxidizing agent selected from the group comprising sodium hypochlorite, sodium peroxide, hydrogen peroxide, and chlorine gas.
30. The method of claim 29, wherein the oxidizing agent is combined with a buffer.
31. The method of claim 30, wherein the buffer is sodium carbonate.
32. The method of claim 1, wherein in the electrowinning step the supernatant is combined with an acid in equal parts to produce an electrolyte bath.
33. The method of claim 32, wherein the acid is sulfuric acid or hydrochloric acid.
34. A method for extracting manganese from an aqueous solution containing iron, comprising the steps of:
 - obtaining a zinc and calcium depleted hydrochloric acid solution containing manganese and iron;
 - removing the iron from the solution by oxidizing the iron, such that the iron precipitates leaving a supernatant containing manganese chloride; and

electrowinning the supernatant in a hydrochloric acid bath, such that electrolytic manganese dioxide forms a deposit.